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TI Lead-free **tin** alloy solder having improved thermal fatigue
characteristic
IN Taki, Hideo; Ogura, Toshiaki; Yoshiura, Yozou; Moribayashi, Toshiyuki
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AB	The Pb-free Sn alloy solder contains Bi 0.1-10, Ag 0.1-5, Cu 0.05-2, Ni 0.0005-0.1, P 0.0005-0.01 and optionally In 0.01-0.5 weight%.				

Table 1
melting temperature

PATENT ABSTRACTS OF JAPAN

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(54) LEAD-FREE SOLDER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lead-free soldering alloy specially having an excellent heat resistant fatigue characteristic and holding as much as possible such a characteristic as a Pb contained soldering alloy in spite of not containing Pb.

SOLUTION: This lead-free solder is composed of, by wt., 0.1-10% Bi, 0.1-5% Ag, 0.05-2% Cu, 0.0005-0.1% Ni, 0.0005-0.01% P and the balance Sn. Also, further, by wt., 0.01-0.5% In is added into this composition. Also, a cream solder containing the powder of the soldering alloy, a formed solder using the soldering alloy and a resin flux cored solder using the soldering alloy are included in this lead-free solder.

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CLAIMS

[Claim(s)]

[Claim 1] The unleaded solder which P 0.0005 - 0.01 % of the weight and the remainder become from Sn 0.1 - 10 % of the weight of Bi(s), 0.1 - 5 % of the weight of Ag, 0.05 - 2 % of the weight of Cu(s), and 0.0005 - 0.1 % of the weight of nickel.

[Claim 2] Furthermore, the unleaded solder according to claim 1 which added 0.01 - 0.5 % of the weight of In (s).

[Claim 3] Cream solder containing the powder of a unleaded solder according to claim 1 or 2.

[Claim 4] Shaping solder using a unleaded solder according to claim 1 or 2.

[Claim 5] the tar using a unleaded solder according to claim 1 or 2 -- entering solder.

[Claim 6] The substrate using a salt-free solder according to claim 1.

[Claim 7] The electronic product using a salt-free solder according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the unleaded solder for soldering which does not contain Pb.

[0002]

[Description of the Prior Art] The alloy which added Pb (lead) to this has been used by using as the base what the conventional solder used Sn (tin) as the base, or blended Sn+Bi (bismuth). Pb carried out the operation which lowers the melting point of 232 degrees C of Sn into an alloy, and the alloy which blended Pb 37% of the weight formed the eutectic solder whose melting point is 183 degrees C, and has been widely used for the suitable melting point. Thus, Pb was an indispensable component in the solder presentation.

[0003] However, if the solder which is an element harmful for men and beasts, and contains Pb is discarded, it is clear that Pb's Pb component causes the serious environmental pollution of beginning to melt gradually by acid rain etc. and permeating into an underground water. In order to respond to the global request that the environmental pollution by such Pb should be prevented, research of the unleaded solder which does not contain Pb is advanced focusing on the solder industry, and many techniques have already been indicated. In these techniques, in order to substitute for work of Pb, they are used by silver (Ag), a bismuth (Bi), antimony (Sb), zinc (Zn), cadmium (Cd), copper (Cu), magnesium (Mg), nickel (nickel), titanium (Ti), the indium (Ti), etc., combining. However, it was not what a poisonous thing and a very expensive thing also have in these elements, and moreover substitutes for the function in which Pb was not necessarily achieved fully.

[0004]

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the unleaded solder excellent in especially the heat-resistant fatigue property which held the property which was moreover also as that of Pb content solder as much as possible excluding Pb.

[0005]

[Means for Solving the Problem] In order that the unleaded solder of this invention may solve the above-mentioned technical problem, the component is characterized by 0.1 - 10 % of the weight of Bi(s), 0.1 - 5 % of the weight of Ag, 0.05 - 2 % of the weight of Cu(s), and 0.0005 - 0.1 % of the weight P 0.0005 - 0.01 % of the weight and the remainder of nickel consisting of Sn. Furthermore, this invention relates to the solder which added 0.01 - 0.5 % of the weight of In(s) to the above-mentioned presentation. moreover, the tar using the cream solder with which this invention contains the powder of the above-mentioned solder, the shaping solder using the above-mentioned solder, and the above-mentioned solder -- entering solder is included.

[0006] The solder of this invention can discover the outstanding property, without completely containing harmful Pb by taking the above-mentioned configuration. The description exerted on the solder property of each configuration element is explained below. It is the principal component of a solder, and Sn does not have toxicity in itself, has the property of excelling in the NURE nature to a junction base material, and is an indispensable component as a solder base material. By adding Ag to Sn, improving a mechanical property and the melting point can be reduced. The loadings of Ag are 0.7 - 3 % of the weight preferably 0.1 to 5% of the weight among a solder. If the effectiveness is insufficient and 5 % of the weight is exceeded when fewer than 0.1 % of the weight, melting temperature will become high and it will become disadvantageous also in respect of cost.

[0007] If Bi is added to what added Ag to Sn, a mechanical strength can improve and melting temperature can be reduced. The loadings of Bi are 0.5 - 5 % of the weight preferably 0.1 to 10% of the weight. Although a mechanical strength will improve if [than 10 % of the weight] more [the effectiveness is insufficient if the

loadings of Bi are lower than 0.1 % of the weight, and], mechanical elongation falls extremely and thermal fatigue tends to occur. If Cu is further added to what added Ag and Bi to Sn, a mechanical strength and fatigue strength-proof are improvable. Cu is added 0.05 to 2% of the weight among a compound. If there is little the effectiveness when fewer than 0.05 % of the weight, and it increases more than 2 % of the weight, melting temperature will rise, on the conventional service condition, it cannot be used and thermal damage is done to the components carried in the substrate.

[0008] Especially the description of this invention is the outstanding manifestation of effectiveness by combination of P and nickel. P can improve the heat-resistant fatigue property and mechanical property (reinforcement and elongation) of solder. And these properties are remarkably improved with the increment in the loadings of P. The loadings of P are 0.0005 - 0.01 % of the weight. Although a mechanical strength will improve if the effectiveness does not have loadings at less than 0.0005 % of the weight and 0.01 % of the weight is exceeded, the surface tension of the fused solder becomes large and a problem arises in NURE in the inside of atmospheric air. Moreover, by adding nickel, it became clear that a heat-resistant fatigue property improved more. The effectiveness becomes much more remarkable by blending nickel with P. The loadings of nickel are 0.0005 - 0.1 % of the weight. When fewer than 0.0005 % of the weight, the effectiveness does not exist, and when [than 0.1 % of the weight] more, the improvement in a thermal fatigue property decreases. In can also improve a heat-resistant fatigue property and a mechanical property. These properties are improved without spoiling other properties by blending In. The loadings of In are 0.01 - 0.3 % of the weight preferably 0.01 to 0.5% of the weight among a solder constituent. If [than 0.5 % of the weight] more [the effectiveness will not show up if fewer than 0.01 % of the weight, and], generation of an oxide increases and it is not desirable. This invention can offer the unleaded solder which excelled the unleaded solder of the conventional Sn-Ag, Sn-Zn, and Sn-Sb system in the thermal fatigue property by setting Sn, Ag, Bi, Cu, nickel, and P as the above-mentioned range.

[0009] What is necessary is just to carry out using the manufacture approach of the usual solder, in order to obtain a solder from the metal raw material of a presentation of this invention. In order to obtain the cream solder containing the solder of this invention, disintegration of the solder is carried out, it considers as powder solder, and solvents, such as suitable resin, such as rosin, glycols, and polyhydric alcohol, are used as a principal component for this, and with the flux which contains additives, such as an activator, a viscosity controlling agent, and an antioxidant, further, it can knead to homogeneity with a conventional method, and can obtain as generally carried out. shaping solder and tar -- it can create by the well-known general approach in the industry of entering solder.

[0010]

[Example]

Example Each metal raw material of the presentation indicated to one to 4 table 1 was fused for 20 minutes at 400 degrees C, and it considered as the uniform alloy. (If it can do, please indicate concretely the manufacture approaches of a typical solder including a melting container, equipment, etc.)

The evaluation approach which shows the obtained alloy below was adopted, and tensile strength and elongation, NURE nature (NURE time amount and NURE stress), and a heat-resistant fatigue property were evaluated. These results were shown in Table 1 and 2.

[0011] Example of a comparison The solder of the examples 1-6 of a comparison was created by the presentation indicated to one to 6 table 1. The property was evaluated like [solder / of the examples 1-6 of a comparison] the example, and the result was shown in Tables 1 and 2.

[0012]

[Table 1]

	はんだ合金組成 (重量%)									溶融 温度	引張	
	S n	B i	A g	C u	N i	P	I n	S b	Z n		強度	伸び
実施例 1	残部	5	2	0.5	0.005	0.001	—	—	—	200 -217	8.35	18.3
実施例 2	残部	5	2	0.5	0.005	0.003	—	—	—		8.60	19.6
実施例 3	残部	5	2	0.5	0.005	0.01	—	—	—		8.78	23.9
実施例 4	残部	5	2	0.5	0.005	0.003	0.2	—	—		8.99	24.2
比較例 1	残部	5	2	0.5	—	—	—	—	—	200 -217	8.21	16.8
比較例 2	残部	5	2	0.5	—	0.003	—	—	—		8.30	18.6
比較例 3	残部	5	2	0.5	0.005	—	—	—	—		8.26	16.1
比較例 4	残部	—	3.5	—	—	—	—	—	—		4.52	24.4
比較例 5	残部	—	—	—	—	—	—	—	9	198	4.58	12.2
比較例 6	残部	—	—	—	—	—	—	5	—	240	3.00	30.0

[0013]

[Table 2]

サイクル数	200	250	300	350	400	450	500
実施例 1	0	1.4	7.1	11.4	17.1	20.0	28.6
実施例 2	0	0	0	2.9	4.3	4.3	4.3
実施例 3	0	0	0	0	2.9	4.3	4.3
実施例 4	0	0	0	0	4.3	5.7	5.7
比較例 1	0	1.4	7.1	11.4	17.1	20.1	28.6
比較例 2	0	0	4.3	12.9	15.7	21.4	21.4
比較例 3	0	0	2.9	5.7	10.0	12.9	15.7
比較例 4	0	1.4	8.5	14.3	21.4	27.1	32.9
比較例 5	0	1.4	5.7	8.6	12.9	17.1	21.4
比較例 6	0	2.9	10.0	15.7	22.9	31.4	34.3

[0014] [The evaluation approach of a solder]

Tensile strength and elongation: The solder was held at 400 degrees C, and it slushed into the mold made from a graphite heated at 270 degrees C, it cooled in a second in 6 degrees C /, and the test piece for tensile test of the configuration shown in drawing 1 was obtained. This test piece was performed in ordinary temperature, the tension test was performed with 5mm speed of testing for /, and it asked for the elongation and reinforcement at the time of fracture.

NURE property (as opposed to copper): Meniscography estimated the NURE time amount and NURE stress in 230-270 degrees C.

NURE time amount : (the appraisal method of NURE time amount, and criterion)

NURE stress : (* * * of NURE stress)

[0015] Thermal-fatigue property: Eight connectors of eight pins were soldered for the solder at 250 degrees C on the 100mmx100mmx1.8mm paper phenol substrate (rear face: copper foil). This installation mode is as being shown in drawing 2. The number of the pin by which +80 degrees C (30 minutes) - -40 degrees C (30 minutes) were made into 1 cycle, this sample was applied to the spalling test, and the crack generated it every 50 cycles up to 500 cycle was investigated. The following formula expressed the crack incidence rate.
(Crack incidence rate) =(number of pin which crack generated)/(the total number of pins)

[0016]

[Effect of the Invention] The unleaded solder of this invention does not contain lead at all, but is excellent in a thermal fatigue property, and its soldering nature is also good.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the unleaded solder for soldering which does not contain Pb.

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PRIOR ART

[Description of the Prior Art] The alloy which added Pb (lead) to this has been used by using as the base what the conventional solder used Sn (tin) as the base, or blended Sn+Bi (bismuth). Pb carried out the operation which lowers the melting point of 232 degrees C of Sn into an alloy, and the alloy which blended Pb 37% of the weight formed the eutectic solder whose melting point is 183 degrees C, and has been widely used for the suitable melting point. Thus, Pb was an indispensable component in the solder presentation.

[0003] However, if the solder which is an element harmful for men and beasts, and contains Pb is discarded, it is clear that Pb's Pb component causes the serious environmental pollution of beginning to melt gradually by acid rain etc. and permeating into an underground water. In order to respond to the global request that the environmental pollution by such Pb should be prevented, research of the unleaded solder which does not contain Pb is advanced focusing on the solder industry, and many techniques have already been indicated. In these techniques, in order to substitute for work of Pb, they are used by silver (Ag), a bismuth (Bi), antimony (Sb), zinc (Zn), cadmium (Cd), copper (Cu), magnesium (Mg), nickel (nickel), titanium (Ti), the indium (Ti), etc., combining. However, it was not what a poisonous thing and a very expensive thing also have in these elements, and moreover substitutes for the function in which Pb was not necessarily achieved fully.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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MEANS

[Means for Solving the Problem] In order that the unleaded solder of this invention may solve the above-mentioned technical problem, the component is characterized by 0.1 - 10 % of the weight of Bi(s), 0.1 - 5 % of the weight of Ag, 0.05 - 2 % of the weight of Cu(s), and 0.0005 - 0.1 % of the weight P 0.0005 - 0.01 % of the weight and the remainder of nickel consisting of Sn. Furthermore, this invention relates to the solder which added 0.01 - 0.5 % of the weight of In(s) to the above-mentioned presentation. moreover, the tar using the cream solder with which this invention contains the powder of the above-mentioned solder, the shaping solder using the above-mentioned solder, and the above-mentioned solder -- entering solder is included.

[0006] The solder of this invention can discover the outstanding property, without completely containing harmful Pb by taking the above-mentioned configuration. The description exerted on the solder property of each configuration element is explained below. It is the principal component of a solder, and Sn does not have toxicity in itself, has the property of excelling in the NURE nature to a junction base material, and is an indispensable component as a solder base material. By adding Ag to Sn, improving a mechanical property and the melting point can be reduced. The loadings of Ag are 0.7 - 3 % of the weight preferably 0.1 to 5% of the weight among a solder. If the effectiveness is insufficient and 5 % of the weight is exceeded when fewer than 0.1 % of the weight, melting temperature will become high and it will become disadvantageous also in respect of cost.

[0007] If Bi is added to what added Ag to Sn, a mechanical strength can improve and melting temperature can be reduced. The loadings of Bi are 0.5 - 5 % of the weight preferably 0.1 to 10% of the weight. Although a mechanical strength will improve if [than 10 % of the weight] more [the effectiveness is insufficient if the loadings of Bi are lower than 0.1 % of the weight, and], mechanical elongation falls extremely and thermal fatigue tends to occur. If Cu is further added to what added Ag and Bi to Sn, a mechanical strength and fatigue strength-proof are improvable. Cu is added 0.05 to 2% of the weight among a compound. If there is little the effectiveness when fewer than 0.05 % of the weight, and it increases more than 2 % of the weight, melting temperature will rise, on the conventional service condition, it cannot be used and thermal damage is done to the components carried in the substrate.

[0008] Especially the description of this invention is the outstanding manifestation of effectiveness by combination of P and nickel. P can improve the heat-resistant fatigue property and mechanical property (reinforcement and elongation) of solder. And these properties are remarkably improved with the increment in the loadings of P. The loadings of P are 0.0005 - 0.01 % of the weight. Although a mechanical strength will improve if the effectiveness does not have loadings at less than 0.0005 % of the weight and 0.01 % of the weight is exceeded, the surface tension of the fused solder becomes large and a problem arises in NURE in the inside of atmospheric air. Moreover, by adding nickel, it became clear that a heat-resistant fatigue property improved more. The effectiveness becomes much more remarkable by blending nickel with P. The loadings of nickel are 0.0005 - 0.1 % of the weight. When fewer than 0.0005 % of the weight, the effectiveness does not exist, and when [than 0.1 % of the weight] more, the improvement in a thermal fatigue property decreases. In can also improve a heat-resistant fatigue property and a mechanical property. These properties are improved without spoiling other properties by blending In. The loadings of In are 0.01 - 0.3 % of the weight preferably 0.01 to 0.5% of the weight among a solder constituent. If [than 0.5 % of the weight] more [the effectiveness will not show up if fewer than 0.01 % of the weight, and], generation of an oxide increases and it is not desirable. This invention can offer the unleaded solder which excelled the unleaded solder of the conventional Sn-Ag, Sn-Zn, and Sn-Sb system in the thermal fatigue property by setting Sn, Ag, Bi, Cu, nickel, and P as the above-mentioned range.

[0009] What is necessary is just to carry out using the manufacture approach of the usual solder, in order to obtain a solder from the metal raw material of a presentation of this invention. In order to obtain the cream solder containing the solder of this invention, disintegration of the solder is carried out, it considers as powder solder, and solvents, such as suitable resin, such as rosin, glycols, and polyhydric alcohol, are used as a principal component for this, and with the flux which contains additives, such as an activator, a viscosity controlling agent, and an antioxidant, further, it can knead to homogeneity with a conventional method, and can obtain as generally carried out. shaping solder and tar -- it can create by the well-known general approach in the industry of entering solder.

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EXAMPLE

[Example]

Example Each metal raw material of the presentation indicated to one to 4 table 1 was fused for 20 minutes at 400 degrees C, and it considered as the uniform alloy. (If it can do, please indicate concretely the manufacture approaches of a typical solder including a melting container, equipment, etc.)

The evaluation approach which shows the obtained alloy below was adopted, and tensile strength and elongation, NURE nature (NURE time amount and NURE stress), and a heat-resistant fatigue property were evaluated. These results were shown in Table 1 and 2.

[0011] Example of a comparison The solder of the examples 1-6 of a comparison was created by the presentation indicated to one to 6 table 1. The property was evaluated like [solder / of the examples 1-6 of a comparison] the example, and the result was shown in Tables 1 and 2.

[0012]

[Table 1]

	はんだ合金組成 (重量%)										溶融	引張	
	Sn	Bi	Ag	Cu	Ni	P	In	Sb	Zn	温度	強度	伸び	
実施例 1	残部	5	2	0.5	0.005	0.001	—	—	—	200	8.35	18.3	
実施例 2	残部	5	2	0.5	0.005	0.003	—	—	—		8.60	19.6	
実施例 3	残部	5	2	0.5	0.005	0.01	—	—	—		-217	8.78	23.9
実施例 4	残部	5	2	0.5	0.005	0.003	0.2	—	—		8.99	24.2	
比較例 1	残部	5	2	0.5	—	—	—	—	—	200	8.21	16.8	
比較例 2	残部	5	2	0.5	—	0.003	—	—	—		8.30	18.6	
比較例 3	残部	5	2	0.5	0.005	—	—	—	—		-217	8.26	16.1
比較例 4	残部	—	3.5	—	—	—	—	—	—	221	4.52	24.4	
比較例 5	残部	—	—	—	—	—	—	—	9	198	4.58	12.2	
比較例 6	残部	—	—	—	—	—	—	5	—	240	3.00	30.0	

[0013]

[Table 2]

サイクル数	200	250	300	350	400	450	500
実施例 1	0	1.4	7.1	11.4	17.1	20.0	28.6
実施例 2	0	0	0	2.9	4.3	4.3	4.3
実施例 3	0	0	0	0	2.9	4.3	4.3
実施例 4	0	0	0	0	4.3	5.7	5.7
比較例 1	0	1.4	7.1	11.4	17.1	20.1	28.6
比較例 2	0	0	4.3	12.9	15.7	21.4	21.4
比較例 3	0	0	2.9	5.7	10.0	12.9	15.7
比較例 4	0	1.4	8.5	14.3	21.4	27.1	32.9
比較例 5	0	1.4	5.7	8.6	12.9	17.1	21.4
比較例 6	0	2.9	10.0	15.7	22.9	31.4	34.3

[0014] [The evaluation approach of a solder]

Tensile strength and elongation: The solder was held at 400 degrees C, and it slushed into the mold made from a graphite heated at 270 degrees C, it cooled in a second in 6 degrees C /, and the test piece for tensile test of the configuration shown in drawing 1 was obtained. This test piece was performed in ordinary temperature, the tension test was performed with 5mm speed of testing for /, and it asked for the elongation and reinforcement at the time of fracture.

NURE property (as opposed to copper): Meniscography estimated the NURE time amount and NURE stress in 230-270 degrees C.

NURE time amount : (the appraisal method of NURE time amount, and criterion)

NURE stress : (** ** of NURE stress)

[0015] Thermal-fatigue property: Eight connectors of eight pins were soldered for the solder at 250 degrees C on the 100mmx100mmx1.8mm paper phenol substrate (rear face: copper foil). This installation mode is as being shown in drawing 2 . The number of the pin by which +80 degrees C (30 minutes) - -40 degrees C (30 minutes) were made into 1 cycle, this sample was applied to the spalling test, and the crack generated it every 50 cycles up to 500 cycle was investigated. The following formula expressed the crack incidence rate.

(Crack incidence rate) =(number of pin which crack generated)/(the total number of pins)

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The flat surface and side elevation showing the test piece configuration for tractive-characteristics evaluation of solder.

[Drawing 2] The sectional view showing the installation mode of the test piece for spalling test evaluation of solder.

[Description of Notations]

1: Solder 2: Land (copper foil)

3: Phenol resin substrate 4: Connector resin

5: Pin

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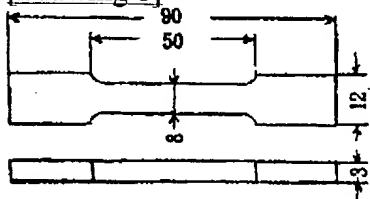
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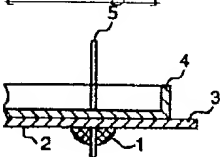
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DRAWINGS

[Drawing 1]



[Drawing 2]



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